FULL LENGTH ARTICLE

Various characteristics of Ni and Pt–Al₂O₃ nanocatalysts prepared by microwave method to be applied in some petrochemical processes

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Abstract  Alumina-supported metal nanocatalysts were prepared via the microwave method, by loading nano Ni particles (at 1, 3 and 5 wt%) or nano Pt particles (at 0.3, 0.6 and 0.9 wt%). Structural and adsorption features of the nano catalysts were revealed through XRD, DSC-DTA, TEM, H₂-chemisorption and N₂-physisorption. N₂-adsorption–desorption isotherms of type IV were related typically to mesoporous materials with H₂ class of hysteresis loops characterizing ink bottle type of pores. The well dispersed nano-sized metal particles were evidenced in the studied catalytic systems, exhibiting marked thermal stability up to 800 °C. The catalytic performances of different catalyst samples were assessed during cyclohexane, normal hexane and ethanol conversions, using the micro-catalytic pulse technique at different operating conditions. The 5% Ni–γ–Al₂O₃ sample was found to be the most active in dehydration of ethanol to produce ethylene, as well as in n-hexane cracking. However, the 1% Ni–Al₂O₃ sample showed the highest dehydrogenation activity for selective production of benzene from cyclohexane. On the other hand, the 0.9% Pt–γ–Al₂O₃ sample exhibited the highest activity in the dehydration of ethanol and in the dehydrogenation of cyclohexane. The 0.3% Pt–γ–Al₂O₃ sample was the most active in the dehydrocyclization of normal hexane, as compared to the other catalyst samples under study.

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1. Introduction

In the last few decades, considerable attention was paid to the nanosized metal colloids and clusters due to their unique properties making them candidates for potential applications in several areas such as catalysis, optoelectronics, microelectronics, photo catalysis, etc. [1–7]. The nanoparticles have a large surface to volume ratio and consequently exhibit increased surface activity as compared to bulk materials [8]. The catalytic
activity of supported metal nanocatalyst is strongly dependent on the shape, size and size distribution of the metal particles [9,10]. Nano-catalysts are highly active since most of the particle surfaces can be available to catalysis. It was assumed that ~60% of the metal atoms exist on the particle surface when its diameter is lower than 3 nm. These surface atoms behave as the centers where the chemical reactions could be catalytically activated. Conventional synthesis methods of small metal particles on inorganic supports have been investigated thoroughly and are well documented [11,12]. Commonly accepted preparation techniques involve ion exchange or impregnation of a support surface with metal salt solutions followed by calcinations and subsequent reduction with hydrogen. However, it is difficult to obtain well-dispersed metal nanoparticles with uniform size distributions. Therefore, considerable effort is focused on developing alternative synthesis methods based on electrochemical reduction, vapor deposition or sonochemistry. Up to now, a great deal of methods for the preparation of metal nanoparticles has been developed, yet, nanoparticles tend to be fairly unstable in solution and therefore, special precautions have to be taken to avoid their aggregation or precipitation during the preparation of such colloidal particles in solution. To obtain stable colloids, the most effective and common strategy is the introduction of a protective agent in the reaction system. In recent years, microwave method has been developed for the preparation of heterogeneous metal colloid catalyst [13]. The microwave method as a heating method has found a number of applications in chemistry since 1986 [14]. Recently, many successes have been reported in using microwave radiation to assist the synthesis of highly pure metallic nanoparticles with narrow size distribution [15,16]. Microwave heating through dielectric losses is fast, uniform and energy efficient. The greatest advantage of microwave is that it can heat a substance directly, leading to a more homogeneous nucleation and shorter crystallization time, compared to conventional heating [17].

Ni/Al2O3 and Pt/Al2O3 nanocatalysts are used in numerous industrial processes in petroleum refining and in petrochemical industries. Supported nickel and platinum are most effectively prepared through the optional combination of high dispersion and metal loading. Small metal particles may be formed on the surface of the support to which they are more or less firmly anchored, and on which they are effectively separated from each other. The average distance between the particles depends on the metal content, the particle size and the surface area of the support [18]. The catalyst efficiency is strongly affected by the preparation process thus to obtain an active and selective catalyst [19]. The higher thermal stability of nickel and platinum can be attributed to a stronger metal support interaction.

The world demand for many petroleum products is increasing every year. One of these products is ethylene which is an essential raw material for petrochemical industry, e.g., PVC industry recently established in Egypt. Also conversion into the corresponding isoparaffins and/or aromatics (by isomerization, hydrogenation, dehydrogenation or dehydrocyclization) is highly required to improve the technical properties of petroleum distillates, e.g., gasoline, jet fuel and diesel oil.

The present work reports the preparation of Ni/Al2O3 and Pt/Al2O3 nanocatalysts using the microwave method. Reduction of nickel and platinum precursors was effected by using hydrazine mono hydrate in ethylene glycol solution in basic media. The as-prepared nanocatalysts were characterized by employing XRD, N2 physisorption, TEM, TGA and DSC techniques. The catalytic activity of different samples was examined in the cyclohexane, n-hexane and ethanol conversions using micro pulse flow system.

2. Experimental

2.1. Material

All the chemicals used were of analytical grade, of 99.9% purity. Nickel nitrate hexahydrate [Ni(NO)3·6H2O] (Fluka) and hexa chloroplatinic acid [H2PtCl6·6H2O] (Merck) were used as precursors for preparation of Ni and Pt nanoparticles, respectively. Sodium hydroxide (NaOH), ethylene glycol (C2H4O2), hydrazine monohydrate (N2H4·H2O), n-hexane, cyclohexane and ethanol (absolute) were used as received.

2.2. Preparation of Ni/Al2O3, Pt/Al2O3 nanocatalysts

A calculated amount of γ-Al2O3 support was impregnated with the solution of each of the precursors used, Ni (NO)3·6H2O or H2PtCl6·6H2O, of certain concentration, in deionized water. The concentrations were calculated such that the loadings of Ni were 1, 3 and 5 wt% and the loadings of Pt were 0.3, 0.6 and 0.9 wt%. Drops of NaOH were added first to the solutions, after which 5 ml of hydrazine mono hydrate was added drop wise, then the mixture was irradiated in a microwave (Kenwood 1100 W and 2450 MHz) for periods of 2 min. The solid products were washed with deionized water and acetone for several times and then washed with absolute ethanol. Finally, the obtained catalysts were dried using vacuum oven at 70°C for 24 h.

The as-prepared catalysts under study were denoted for Ni/Al2O3 nanocatalysts of different loadings as 1 Ni–Al, 3 Ni–Al and 5 Ni–Al, and for Pt/Al2O3 nanocatalysts of the corresponding loadings as 0.3 Pt–Al, 0.6 Pt–Al and 0.9 Pt–Al.

2.3. Characterization

The textural characteristics of the prepared nanocatalysts were characterized by the aid of N2 adsorption–desorption isotherms at −196°C using a NOVA 3200 apparatus, USA. The samples were pretreated under vacuum (10−4 Torr) at 300°C for 24 h. Surface areas (SBET) were calculated by applying BET equation from the adsorption branch. Particle size distributions were calculated using the Barrett, Joyner and Halenda (BJH) method from desorption branch of the isotherms [20].

Powder X-ray diffraction was recorded on a Brucker D8 advance X-ray diffractogram with Cu Kα radiation (λ = 1.5418 Å). DSC-TGA analyses were carried out for all supported nanocatalyst samples using simultaneous DSC-TGA SDTQ 600, USA under N2 atmosphere, with a heating rate of 10°C min−1. The morphology as well as the metal dispersions of the reduced metal catalysts was analyzed by JEOL TEM-1230 Electron microscope, 120 Kw, 600,000 magnifications, Japan.

Catalytic activity of Ni–Al and Pt–Al nanocatalysts was tested through n-hexane, cyclohexane and ethanol conversions...
as three model reactions using a micro catalytic pulse technique attached to data acquisition. The reactor effluent was passed through a chromatographic column for separation and determination of the products using flame ionization detector (FID) connected to computerized data acquisition station. The column of 200 cm length and 0.3 cm internal diameter was used containing acid-washed PW chromosorb (60–80 mesh size) loaded by 15% by weight squalane. The reactions were carried out under atmospheric pressure in the temperature range, 250–450 °C. Hydrogen flow rate was kept constant at 50 ml min⁻¹. Prior to catalytic activity runs, the reduced catalyst samples were heated in H₂ flow for 2 h at 450 °C for activation. Few doses of reactants were injected first to reach the steady state of the reaction. The chromatographic column temperature was adjusted and controlled at 50 °C.

3. Results and discussion

3.1. Textural characteristics

Surface characteristics of various Ni–Al and Pt–Al nanocatalysts of different metal loadings were studied through N₂ adsorption-desorption isotherms at −196 °C, as depicted in Figs. 1(a) and 2(a). Pore analysis was carried out by applying

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**Figure 1**  (a) N₂ adsorption–desorption isotherms of alumina and Pt/alumina Prepared by Microwave Method. (b) Pore size distribution curve of alumina and Pt/alumina Prepared by Microwave Method.

**Figure 2**  (a) N₂ adsorption–desorption isotherms of alumina and Ni/alumina Prepared by Microwave Method. (b) Pore size distribution curve of alumina and Ni/alumina Prepared by Microwave Method.
the BJH method, where the pore size distribution (PSD) curves are illustrated in Figs. 1(b) and 2(b).

It is evident that the obtained adsorption–desorption isotherms for both kinds of nanocatalysts are of type IV, being mainly characteristic for mesoporous materials [20]. They are all associated with H2 type of hysteresis loops, in the relative pressure (p/p0) range of 0.60–0.99, usually related to the ink-bottle pores with wide orifice of the border inner parts. The obtained isotherms for the supported Pt and Ni catalysts display almost the same behavior as that of pure Al2O3 support, which may be linked with nanosized metal particles and/or their high dispersion. The total N2 uptake seems to decrease gradually with increasing the % loading of Ni and Pt, indicating less accessibility of surface for N2 molecules. Table 1 summarizes the different surface data derived from the adsorption isotherms. Both the specific surface area (SBET) of 141.46 m² g⁻¹ and total pore volume (Vp) of 0.2963 cm³ g⁻¹ of pure Al2O3 support seem to decrease gradually with increasing the % loading of Pt nanoparticles up to 0.6 wt%. This is accompanied with appearance of a group of narrower mesopores (of most probable hydraulic pore diameter, D = 3.82 nm) in the PSD curves beside the original mesopores of the alumina support of D = 5.62 nm (Fig. 1b). Such bimodal PSD may be related to the incorporation of a fraction of Pt nanoparticles, less accessible, in the alumina pore system. However, for 0.9 Pt–Al nano-catalyst, some relative increase in both SBET and Vp parameters is observed, probably associated with some pore widening, i.e., with increased D value to 6.36 nm, and probable blocking of the narrower fraction of mesopores. Here, the unimodal PSD may indicate the transfer of some of Pt nanoparticles to the top surface of the alumina pore system, i.e., with more accessibility to the reaction environment.

Also, for Ni–Al nanocatalysts, both SBET and Vp parameters of the neat Al2O3 support are considerably decreased upon loading with 1.0 wt% Ni. This may be related to the deeper incorporation of a great deal of nanosized Ni particles in the alumina pore system, as revealed by creation of narrower fraction of pores of D = 3.81 nm beside the original mesopores of the alumina support of D = 5.62 nm (Fig 2b). By increasing the Ni loading to 3.0 and 5.0 wt%, an increase is observed in SBET and Vp parameters, as in 0.9 Pt-Al, maintaining the same narrower fraction of pores (of D = 3.81 nm). Generally, the bimodal PSD that occurred for all the studied Ni–Al catalysts may be linked with smaller particle sizes of incorporated Ni nanoparticles, seeming to be mobile in the interior pore structure.

3.2 XRD analysis

The XRD patterns of in situ reduced Pt and Ni-based γ-Al2O3 nanocatalysts are presented in Fig. 3(a) and (b). For the pure alumina support, formation of poorly crystallized phase is evident from the broad peaks indexed for γ-Al2O3 in the obtained patterns (Fig. 3, with planes of cubic-like phase). The characteristic features of γ-Al2O3 (JCPDS 75-0921) can be noticed in all samples of the studied Ni–Al and Pt–Al nanocatalysts in their reduced state. However, for Ni-based catalyst samples, new diffraction lines at 44° (111) and 51.6° (200) could be detected, being characteristics of reduced Ni phase (JCPDS 04-850). Also, in Pt-containing catalyst samples, small diffractions lines were detected at 39.8° (111), 46.5° (200) and 67.8° (220), which can be attributed to a Pt metallic phase (JCPDS 01-1190) [21–23]. The broad peaks with
lower intensity represented in both investigated catalysts indicate that the nanosized metallic particles are well dispersed in an almost amorphous or poorly crystalline structure. These results may point to the effectiveness of the reduction profile applied by using hydrazine hydrate in the microwave conditions. Moreover, as only a low temperature (viz., 70 °C) was used, without any calcination treatment, formation of new structural coordination compounds between alumina support and the active metals under study was not expected. Actually, no diffraction lines related to metal-support interaction (in form of aluminate spinels) could be identified. These findings should be evidenced through TGA and TEM investigation as will be discussed below. This should also be reflected on the activity pattern of the used nanocatalytic systems.

3.3. Thermal analysis

In order to reveal the changes that might occur during heat treatment of the solid powders, TGA and DSC analyses were carried out from 25 to 1000 °C under N2 atmosphere (Figs. 4 and 5). According to the TG curves of Pt–Al and Ni–Al catalysts, the major part of the weight loss seems to occur below

![Figure 4](https://example.com/figure4.png)

**Figure 4** (a) DSC of (A) alumina and Pt/alumina with different platinum percentages: (B) 0.3%, (C) 0.6% and (D) 0.9%. (b) TGA of (A) alumina and Pt/alumina with different platinum percentages: (B) 0.3%, (C) 0.6% and (D) 0.9%.
200 °C, most probably corresponding to the elimination of the absorbed water as observed in the neat alumina support. This is confirmed by the endothermic peak in this region in all the obtained DSC curves (Figs. 4b and 5b). Another endothermic peak can be observed in the range of 400–600 °C, accompanied with some weight loss, almost linked with progressive decomposition of the residual precursors and/or probable structural reorganization of alumina support. For instance, for 0.6 Pt–Al and specifically 0.9 Pt–Al, although more pronounced loss of physically adsorbed water is observed in the first step, the slight weight loss in the second step seems to be linked with reorganization of the stronger interaction structure of the nano-catalytic system. However, for Ni–Al nanocatalysts, specifically the 5Ni–Al sample, this second stage evidently splits into two steps, viz., 220–350 °C, likely tied with decomposition of the residual precursor and 350–600 °C, indicating more facile reorganization of the interaction system, involving highly mobile dispersed Ni nanoparticles with support surface.

Figure 5  (a) DSC of (A) alumina and Ni/alumina with different nickel percentages: (B) 1%, (C) 3% and (D) 5%. (b) TGA of (A) alumina and Ni/alumina with different nickel percentages: (B) 1%, (C) 3% and (D) 5%.
Moreover, the obtained thermogravimetric patterns did not show any exothermic peak above 900 °C, related to dehydration or transformation of γ-alumina to inactive α-alumina phase. Generally, the

<table>
<thead>
<tr>
<th>Catalyst name</th>
<th>Dispersion</th>
<th>Avg. crystallite size area (Å)</th>
<th>Surface area/g of metal m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 Pt–Al</td>
<td>0.716</td>
<td>3.95</td>
<td>707.96</td>
</tr>
<tr>
<td>0.6 Pt–Al</td>
<td>0.530</td>
<td>8.91</td>
<td>317.05</td>
</tr>
<tr>
<td>0.9 Pt–Al</td>
<td>0.402</td>
<td>7.03</td>
<td>397.74</td>
</tr>
<tr>
<td>1 Ni–Al</td>
<td>0.011</td>
<td>226.7</td>
<td>29.7</td>
</tr>
<tr>
<td>3 Ni–Al</td>
<td>0.040</td>
<td>63.71</td>
<td>105.8</td>
</tr>
<tr>
<td>5 Ni–Al</td>
<td>0.002</td>
<td>455.76</td>
<td>6.14</td>
</tr>
</tbody>
</table>
thermal stability of the nanocatalytic systems under study up to 1000 °C may favor the preparation and reduction processes under microwave conditions. This can be more confirmed from morphology investigation by the TEM technique.

3.4. TEM micrographs

TEM micrographs of pure γ-alumina support as well as the Pt-Al and Ni-Al nanocatalysts of different metal loadings are illustrated in Fig. 6.

Fig. 6(a1) depicts the TEM image of γ-alumina exhibiting a nanostructure, where the average particle size ranges between 5 and 10 nm. The image 6(a2) shows disordered arrays of nanoflakes. TEM images of Pt-Al samples are represented in Fig. 6(b–d), where Pt nanoparticles are well dispersed on the outer surface of alumina nanoflakes. Of special interest are the 0.6Pt–Al samples; where regular distribution of Pt particles, of average sizes ≤5 nm, on organized arrays of alumina nanoflakes becomes more pronounced (c1). The interaction of Pt nanoparticles with γ-alumina nanoflakes can lead to more facile organization of the support array, while the metal nanoparticles become highly dispersed (c2) in accordance with the five alumina planes (XRD, Fig. 1). They are well distributed in a controlled mobilization in a lattice spacing of

Figure 7  Catalytic conversion of n-hexane over Pt/alumina with different Pt loadings: (A) 0.3%, (B) 0.6% and (C) 0.9% by Microwave Method.
~0.2 nm, corresponding to (222) plane of γ-Al₂O₃ (HRTEM, Fig. 6, c3). The TEM images in Fig. 6(e–g) of Ni–Al catalyst samples of different loadings show better dispersions of Ni nanoparticles of much less than 5 nm average sizes, almost covering the whole alumina surface.

These observations confirm, in general, the effectiveness of the reduction method by microwave tool to generate stable platinum and nickel well dispersed nanoparticles, with average sizes not exceeding 5 nm even with increasing Pt and Ni loading.

3.5. Hydrogen chemisorptions

From the obtained H₂-chemisorption measured at ambient temperature, the dispersion parameters were derived and summarized in Table 2.

It is clear that the supported Pt catalyst samples were characterized by their higher dispersion nature and consequently less sized Pt metal particles. On the other hand, in the supported Ni Samples, the Ni particles seemed to exist in aggregates of larger dimensions. The degree of Ni dispersion on the surface was therefore; much lower than in the Pt catalyst. Metallic surface areas in this case are much smaller than these of the supported Pt catalyst.

3.6. Catalytic performances

3.6.1. n-Hexane conversion

In the present work, the hydroconversion of n-hexane has been investigated using Ni-Al and Pt-Al nanocatalysts at 350–450 °C. The hydroconversion of n-paraffins includes hydroisomerization, hydrocracking and dehydrocyclization reactions.

The catalytic performance of Pt–Al system (Fig. 7) shows mainly the dehydro-cyclization of n-hexane reaction. This may be accepted in view of the fact that alumina support contains strong basic sites [24] that may favor the dehydrocyclization or aromatization of n-hexane. The catalytic activity of Pt–Al samples toward dehydro-cyclization (aromatization) increases with increasing the reaction temperature in the

![Figure 8](image)

**Figure 8** Catalytic conversion of n-hexane over Ni/alumina with different Ni loadings: (A) 1%, (B) 3% and (C) 5% by Microwave Method.
following order: 0.3 Pt–Al ≈ 0.9 Pt–Al > 0.6 Pt–Al. The selectivity to benzene formation reaches 100% over the whole range of the reaction temperatures (Fig. 7) by using 0.3% and 0.6% Pt–Al catalysts. Yet, it achieves only 73% at 450 °C when using 0.9 Pt–Al, due to formation of by-products. The cracking of \( n \)-hexane is shown to take place only on 0.9 Pt–Al catalyst sample, as compared with other samples. The yield of cracking products increases with increasing the reaction temperature, reaching 17% at 450 °C. This may indicate that Pt nanoparticles cover the weaker acidic centers of alumina support, leaving the strongest Lewis acid centers available for C–C bond hydrogenolysis.

Catalytic conversion of \( n \)-hexane over Ni–Al catalysts of 1, 3 and 5 wt% Ni at reaction temperatures, 300–450 °C, is illustrated in Fig. 8. All Ni–Al samples are considered as active and selective for \( n \)-hexane cracking [25], where the total conversion and the cracking yield increase with both the reaction temperature and the % loading of Ni. The selectivity of \( n \)-hexane cracking has reached 100% over the whole range of the temperatures (Fig. 8). It is worth mentioning that alumina support itself has strong Lewis acid sites responsible for the high cracking activity [26].

**3.6.2. Cyclohexane conversion**

Catalytic conversion of cyclohexane over Pt–Al catalyst samples containing 0.3, 0.6 and 0.9 wt% Pt is shown in Fig. 9. The results reveal that, the total conversion increases by increasing the reaction temperature in the range, 300–450 °C. The catalytic activity for cyclohexane dehydrogenation increases by increasing Pt content. Benzene yield (mole%) sharply increases with the temperature and reaches 100% at 350 °C for the sample 0.9 Pt–Al, compared with the other samples namely; 0.3 and 0.6 Pt–Al where their benzene yields are 53% and 56%, respectively. The benzene yields on 0.3 and 0.6 Pt–Al samples reach 100% at 400 °C. For 0.9 Pt–Al catalyst sample, in addition, a low yield of \( C_6 \) isomers is detected in chromatographic analysis of cyclohexane isomerization. The selectivity of benzene formation achieves the maximum value of 100% over the whole range of the temperatures (Fig. 9), which runs in line with the Zelinsky reaction and thermodynamics feasibility [27,28]. No cracking side reaction could be detected under the applied conditions. This can be linked with the TEM results (Fig. 6), where the operating fraction of Pt is interacting with the defective octahedral sites of alumina seems

![Figure 9](image_url)  
**Figure 9** Catalytic conversion of cyclohexane over Pt/Alumina with different Pt loadings: (A) 0.3%, (B) 0.6% and (C) 0.9% by Microwave Method.
to be increased with Pt loading and with temperature. It is known that this octahedrally sited fraction in the surface layer of the catalyst is active and easily reducible. 0.9 wt% Pt can be considered as selective one for dehydrogenation reaction of cyclohexane.

Catalytic conversion of cyclohexane over Ni–Al catalysts, of 1, 3 and 5 wt% Ni, shows an increase in the total conversion with temperature in the range of 300–450 °C (Fig. 10). The yield of benzene increases with temperature reaching to a maximum at 350 °C and then declines due to the appearance of gaseous cracking products. At 350 °C, the mole% of benzene is almost the same for both 1% and 3% Ni–Al catalysts (viz., 34%), but it decreases for the 5 Ni–Al sample (24%) due to increasing the side reactions. Both the yield and the selectivity of cyclohexane cracking are increased at the expense of benzene formation by increasing the reaction temperature and the Ni content.

The cracking yield reaches 24%, 50% and 90% at 450 °C for 1, 3 and 5 wt% Ni, respectively, which goes in line with thermodynamic feasibility [29]. In addition, a low yield due to C₆ isomers is detected in chromatographic analysis of cyclohexane isomerization over 0.6 and 0.9 Pt–Al catalyst samples. In general, Ni–Al samples are shown to be selective cracking catalysts. This may suggest that supported Ni nanoparticles seem to cover the fraction of weak acid sites of alumina support, exposing thereby the major fraction of stronger acid sites available for the cracking pathway of the conversion reaction [30].

**3.6.3. Ethanol conversion**

Ethanol dehydration into ethylene was also tested in the present work for catalytic activity measurement of Pt and Ni nanocatalysts under investigation. The dehydration is often accompanied by dehydrogenation during the catalytic decomposition of alcohols such as ethanol and isopropanol. It has been reported that the selectivity to acetaldehyde, yielded through ethanol dehydrogenation, can reach 100% when the reaction temperature is controlled below 300 °C [31–33]. With temperatures above 300 °C, the predominant product of

![Figure 10](image_url)  
**Figure 10** Catalytic conversion of cyclohexane over Ni/Alumina with different Ni loadings: (A) 1%, (B) 3% and (C) 5% by Microwave method.
dehydration is mainly ethylene and water, while below 300 °C, diethyl ether and water are predominant in addition to dehydrogenation of ethanol to acetaldehyde [34,35].

The results of ethanol conversion and yields (mole%) of ethylene and acetaldehyde over Pt–Al and Ni–Al nanocatalysts are illustrated in Figs. 11 and 12. All catalysts used exhibited remarkable activity toward both dehydration and dehydrogenation of ethanol. The reaction of ethanol dehydration to ethylene over Ni–Al nanocatalyst starts at 150 °C, while over Pt–Al nanocatalyst it starts at 300 °C. Using the two catalyst systems, the obtained activity parameters, viz., total conversion of ethanol, yield and selectivity to ethylene increase with rising the reaction temperature (Figs. 11 and 12). Ethanol total conversion is nearly 100% at 450 °C with lower metal loadings; (0.3% and 0.6%) Pt–Al and (1%) Ni–Al nanocatalysts and is 100% at 350–450 °C with higher metal loading; (0.9%) Pt–Al and (3% and 5%) Ni–Al nanocatalysts. This may indicate that the ethanol conversion depends on the % of metal loading.

The maximum yield (mole%), i.e., the selectivity to ethylene obtained over all investigated catalysts is found to be 61%. This maximum value (61%) is achieved over all Ni–Al catalyst samples, of different Ni contents, as well as the 0.3 and 0.9 Pt–Al samples at 450 °C. With 0.6 Pt–Al sample, an activity...
value (58%) is reached at 450 °C. Ethanol dehydrogenation increases with reaction temperature reaching its maximum level at 350 °C then it declines. The yield of acetaldehyde, however, slightly increases with increasing the Pt content and reaching to 20%, 21% and 22% for 0.3%, 0.6% and 0.9% Pt, respectively. Over Ni–Al catalysts, acetaldehyde yield reaches 17% over 1 and 3 Ni–Al and 23% on 5 Ni–Al catalyst samples. Moreover, with Pt catalyst samples containing ≤0.6 wt% Pt, low yield of diethyl ether is observed as a result of ethanol dehydrogenation.

As for the mechanism of ethanol dehydration, Hassan [36] suggested that ethanol firstly adsorbs on the acid center of the catalyst surface and then forms an oxonium ion C₂H₅OH²⁺, which either reacts with another C₂H₅OH molecule to form the foremost product of diethyl ether or through dehydration it forms the ethylene. The moderate acid site on the surface of the catalyst has an important influence on the catalytic dehydration performance of ethanol [37] as shown in scheme 1 [38].

4. Conclusions

The prepared Pt- and Ni-based γ-Al₂O₃ nanocatalysts through the microwave technique were composed of metal nanoparticles supported on alumina nanoflakes as confirmed through several techniques. These nanocatalytic systems have been...
proved to be highly stable and active in cyclohexane dehydrogenation, \( n \)-hexane cracking and ethanol dehydration. Pt–Al catalysts were selective for benzene production from cyclohexane dehydrogenation taking place mainly on the metallic nanoparticles existed at octahedral sites of the support. Ni–Al samples were shown to be selective cracking catalysts. Supported Ni nanoparticles seemed to cover a fraction of weak acid sites of alumina support, exposing thereby the major fraction of stronger acid sites available for cracking pathway of the reaction. All the studied catalytic systems exhibited high activity and selectivity to ethylene formation with maximum selectivity (100%) at 450 °C.

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